X-ray Resonant Magnetic Scattering : Polarisation Dependence in the non-spherical case.

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Abstract. We develop a simple tensorial contraction method to obtain analytical formula for X-ray resonant magnetic scattering. We apply the method considering first electric dipole-dipole and electric quadrupole-quadrupole scattering in the isolated atom approximation and compare the results with previous works. Then we apply the method to derive phenomenological original formulas which account also for non-spherical systems and for dipole-quadrupole mixing.

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1 INTRODUCTION

X-ray magnetic scattering exhibits huge enhancement at resonances corresponding to localized electronic states[1,2]. Because of its coherent nature and dependence on polarisation, X-ray resonant magnetic scattering (XRMS) can be used to determine both spatial distribution and orientation of matter magnetisation.

To design experiments and analyse data, there is a strong need for simple analytical formula which directly relate the experimental geometry and sample orientation to the measured scattered intensity.

Simple formula for RMXS amplitude can be found in the literature with the approximation of spherical atoms[3].

They are composed of a sum of terms, each term being the product of a geometrical expression, containing polarisations, multiplied by a complex valued function of energy. In a phenomenological analysys, where one is interested in separating the different contributions to the spectra, one can take theses complex valued function as free parameters, under the constraint that dispersion relation are satisfied.

We derive a simple and understandable theoretical framework within which we recover previous XRMS formula and then we extend such formula to non-spherical systems.

2 introduction to scattering factors

The interaction between matter and a photon described by a wave vector k and polarisation ϵ, is written, discarding elastic Thomson scattering (the $A^2(r)$ term in the Schroedinger equation which becomes dominant off-resonance), and discarding also the spin-magnetic field interaction [4] , as :

$$H_{int} = \tag{1}$$

$$\left(\frac{2\pi\hbar c^2}{\omega V}\right)^{1/2} (a^\dagger_{k,\epsilon} exp(-i\mathbf{k}\cdot\mathbf{r}) + a_{k,\epsilon} exp(i\mathbf{k}\cdot\mathbf{r}))\frac{e}{cm}\mathbf{p}\cdot\epsilon \tag{2}$$

where r is the electron coordinate, p the kinetic moment, $a^\dagger_{k,\epsilon}$, $a_{k,\epsilon}$ are creation annihilation photon operators, $\omega = kc$, and V is the space volume.

The photon-photon resonant scattering is a second order perturbative process whose resonating amplitude per unit of time, for initial ϵ, k and final ϵ', k' states, is obtained from H_{int} matrix elements as :

$$t_{\epsilon k\to\epsilon'k'} = -i\frac{2\pi e^2}{\hbar\omega m^2 V}\sum_n \frac{\left\langle 0|e^{-i\mathbf{k}'\cdot\mathbf{r}}\mathbf{p}\cdot\epsilon'|n\right\rangle\left\langle n|e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{p}\cdot\epsilon|0\right\rangle}{\omega - \omega_n + i\delta} \tag{3}$$

where $< n|$ is a complete set of eigenstates of matter, $< 0|$ being the initial state, $\hbar\omega_n$ is the energy difference between $< n|$ and $< 0|$ and we have retained only the resonating denominator. In the literature one always finds the scattering amplitude $F_{\epsilon k\to\epsilon'k'}$ which is related to the

above equation by the following definition where one has factored out a $icr_0\lambda/V$ factor (r_0 is the classical radius of the electron) :

$$t_{\epsilon k\to\epsilon'k'} = ic/V r_0\lambda F_{\epsilon k\to\epsilon'k'} \tag{4}$$

or

$$F_{\epsilon k\to\epsilon'k'} = \frac{1}{\hbar m}\sum_n \frac{\left\langle 0|e^{-i\mathbf{k}'\cdot\mathbf{r}}\mathbf{p}\cdot\epsilon'|n\right\rangle\left\langle n|e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{p}\cdot\epsilon|0\right\rangle}{\omega - \omega_n + i\delta} \tag{5}$$

this formula is the starting point of our analysys. To analyse such formula we expand $exp(ik\cdot r)p\cdot\epsilon$ to first order, and rewrite the electron momentum $\mathbf{p}$ as $\frac{im}{\hbar}[H,\mathbf{r}]$:

$$exp(ik\cdot r)p\cdot\epsilon \simeq (1 + ik\cdot r)\frac{im}{\hbar}[H, r\cdot\epsilon] \tag{6}$$

$$= [H, r\cdot\epsilon] + i[H, k\cdot rr\cdot\epsilon]/2$$

where the exponential has been expanded up to first order and H is the system Hamiltonian. Such substitution leads to :

$$F_{\epsilon k\to\epsilon'k'} =$$

$$\frac{m}{\hbar}\sum_n \frac{\omega_n^2\left\langle 0|(\epsilon'\cdot r - \frac{i}{2}k'\cdot r\epsilon\cdot r)|n\right\rangle\left\langle n|(\epsilon\cdot r + \frac{i}{2}k\cdot r\epsilon\cdot r)|0\right\rangle}{\omega - \omega_n + i\delta} \tag{7}$$

As we are going to describe atoms as spherical entities plus some kind of distortion it is interesting to consider the spherical group and how the angular part of the different terms of Eq. 6 decompose on the irreducible representations of such a group. The scalar product $\epsilon\cdot\mathbf{r}$ can be rewritten as a sum of products of rank 1 spherical harmonics tensors components :

$$\epsilon\cdot\mathbf{r} = \sum_{q=-1}^{q=+1}\epsilon_q^{1*}r_q^1 \tag{8}$$

where, given a cartesian vector $\mathbf{A}$, its spherical tensor components are

$$A_0^1 = A_z$$

$$A_1^1 = -(A_x + iA_y)/\sqrt{(2)}$$

$$A_{-1}^1 = (A_x - iA_y)/\sqrt{(2)}.$$

$$(9)$$

The product $\mathbf{k} \cdot \mathbf{r}\epsilon \cdot \mathbf{r}$ is the sum of a constant contribution (rank 0) and a sum of products of rank 2 spherical harmonics tensors:

$$(\mathbf{k} \cdot \mathbf{r})(\epsilon \cdot \mathbf{r}) = \frac{1}{3}(\mathbf{k} \cdot \epsilon)(\mathbf{r} \cdot \mathbf{r}) + \sum_{q=-2}^{q=+2} (k\epsilon)_q^*(rr)_q \qquad (10)$$

where, given two cartesian vectors $\mathbf{A}$ and $\mathbf{B}$, the symbols $(\mathbf{AB})_q$ denote the rank 2 spherical symmetric tensor components of their product which are :

$$(\mathbf{AB})_0 = \frac{1}{\sqrt{6}}(2A_zB_z - A_xB_x - A_yB_y)$$

$$(\mathbf{AB})_{\pm 1} = \mp\frac{1}{2}(A_xB_z + A_zB_x \pm i(A_yB_z + A_zB_y))$$

$$(\mathbf{AB})_{\pm 2} = \frac{1}{2}(A_xB_x - A_yB_y \pm i(A_xB_y + A_yB_x))$$

$$(11)$$

We see from Eq. 10 that spherical tensorial components of the tensor product $\mathbf{k} \otimes \epsilon$ are coupled to same rank components of the product $\mathbf{r} \otimes \mathbf{r}$ to form a scalar. As the product $\mathbf{r} \otimes \mathbf{r}$ has no antisymmetric component the rank 1 components of the product $\mathbf{k} \otimes \epsilon$ do not appear in Eq. 10.

The transformations expressed by Eqs. 9,11 are used to simplify the scattering factor expression by choosing the angular moment quantisation axis in the most appropriate way. In the next section we consider a spherical system pertubed by a magnetic exchange interaction

while in section 4 we consider a non-spherical perturbation term and derive a phenomenological expression for the magnetic scattering amplitude.

3 derivation of formula for the spherical case with a magnetic field perturbation

In the case of a spherical atom perturbed by a magnetic exchange field the final scattering amplitude expression does not mix dipolar with quadrupolar terms because of parity conservation. We take the angular moment quantisation axis $\hat{\xi}$, along the magnetic field. Terms having different quantisation number q will not mix. The expression for scattering then assumes the following simple form :

$$F_{\epsilon k \to \epsilon' k'} = \sum_{q=-1}^{q=1} F_{1,q}\epsilon_q^{1*}\epsilon_q^1 + \sum_{q=-2}^{q=2} F_{2,q}(k\epsilon)_q^*(k\epsilon)_q \qquad (12)$$

In the spherically symmetric case (no magnetic field) the $F_{1,q}$ and $F_{2,q}$ are independent of q. The introduction of a magnetic field introduces a q dependence in the scattering factors that can be expanded as a polynomial in the quantisation number q :

$$F_{1,q} = F_1^0 + qF_1^1 + q^2F_1^2$$

$$F_{2,q} = F_2^0 + qF_2^1 + q^2F_2^2 + q^3F_2^3 + q^4F_2^4$$

$$(13)$$

Where the coefficients are given by :

$$F_1^{0\prime} = F_{1,0}$$

$$F_1^{1\prime} = (F_{1,1} - F_{1,-1})/2$$

$$F_1^{2\prime} = (2F_{1,0} - F_{1,1} - F_{1,-1})/2$$

$$F_2^{0\prime} = F_{2,0}$$

$$F_2^{1\prime} = (F_{2,-2} - F_{2,2} + 8F_{2,1} - 8F_{2,-1})/12$$

$$F_2^{2\prime} = (16F_{2,1} + 16F_{2,-1} - F_{2,-2} - F_{2,2} - 30F_{2,0})/24$$

$$F_2^{3\prime} = (F_{2,2} - F_{2,-2} + 2F_{2,-1} - 2F_{2,1})/12$$

$$F_2^{4\prime} = (6F_{2,0} - F_{2,2} - 2F_{2,-2} - 4F_{2,1} - 4F_{2,-1})/24$$

$$(14)$$

In the non magnetic case all the terms are zero except the zero order ones.

We can substitute q in Eq. 12 by $\hat{\xi}.\mathbf{L}$ where $\mathbf{L}$ is the angular moment operator. Going back to cartesian space, Eq. 12 is then written as

$$F_{\epsilon k \to \epsilon' k'} = \mathbf{C} \left(\epsilon' \sum_{n=0}^{n=2} (i\hat{\xi}\times)^n F_1^{\prime n} \epsilon \right) +$$
$$\mathbf{C} \left(\mathbf{k}' \otimes \epsilon' \sum_{n=0}^{n=4} (i\hat{\xi}\times)^n F_2^{\prime n} \mathbf{k} \otimes \epsilon \right)/2$$

$$(15)$$

where the symbol $\mathbf{C}$ means the sum of all possible contractions of the two vectors ϵ' and $\mathbf{k}'$ with the expression to their right. A contraction is realised by coupling by pairs the $2N$ vectors which enter the expression , where $2N$ is the sum of the tensors ranks. Each vectors couple is then contracted, the result being the scalar product, and the N scalar products are multiplied together to give the final result. The contraction of a tensor of defined rank with itself must not be considered.

For dipolar scattering we have therefore

$$F_{\epsilon\mathbf{k}\to\epsilon' k'}^{dipolar} = \epsilon'\cdot\epsilon F_1^{\prime 0} + \epsilon'\cdot(i\hat{\xi}\times\epsilon)F_1^{\prime 1} + \epsilon'\cdot(i\hat{\xi}\times i\hat{\xi}\times\epsilon)F_1^{\prime 2} \quad (16)$$

such formula can be rearranged in the Hill & Mc Morrow [3] form :

$$F_{\epsilon k\to\epsilon' k'}^{dipolar} = \epsilon'\cdot\epsilon(F_1^{\prime 0} - F_1^{\prime 2}) - i\hat{\xi}\cdot(\epsilon'\times\epsilon)F_1^{\prime 1} + (\epsilon'\cdot\hat{\xi})(\epsilon\cdot\hat{\xi})F_1^{\prime 2}$$

$$(17)$$

For the quadrupolar term the same procedures apply with some more bookkeeping for the various terms that arise when we apply the $i\hat{\xi}\times$ operator on the right terms. In details :

$$(i\hat{\xi}\times)^0 \epsilon \otimes \mathbf{k} = \epsilon \otimes \mathbf{k}$$

$$(i\hat{\xi}\times)^1 \epsilon \otimes \mathbf{k} = i(\hat{\xi}\times\epsilon)\otimes\mathbf{k} + i\epsilon\otimes(\hat{\xi}\times\mathbf{k})$$

$$-(\hat{\xi}\times)^2 \epsilon \otimes \mathbf{k} = \epsilon_\perp\otimes\mathbf{k} - 2(\hat{\xi}\times\epsilon)\otimes(\hat{\xi}\times\mathbf{k}) + \epsilon\otimes\mathbf{k}_\perp$$

$$-i(\hat{\xi}\times)^3 \epsilon \otimes \mathbf{k} = i(\hat{\xi}\times\epsilon)\otimes\mathbf{k} + 3i\epsilon_\perp\otimes(\hat{\xi}\times\mathbf{k})$$
$$+ 3i(\hat{\xi}\times\epsilon)\otimes\mathbf{k}_\perp + i(\hat{\xi}\times\mathbf{k})\otimes\epsilon$$

$$(\hat{\xi}\times)^4 \epsilon \otimes \mathbf{k} = \epsilon_\perp\otimes\mathbf{k} - 8(\hat{\xi}\times\epsilon)\otimes(\hat{\xi}\times\mathbf{k})$$
$$+ 6\epsilon_\perp\otimes\mathbf{k}_\perp + \mathbf{k}_\perp\otimes\epsilon$$

$$(18)$$

Each of the terms of the above equation must be multiplied by its own $F_2^{\prime q}$ and contracted with $\epsilon'\mathbf{k}'$. The result

is :

$$F_{\epsilon k \to \epsilon' k'}^{quadrupolar} = (F_2'^0 + 2F_2'^2 + 8F_2'^2)S(\epsilon' \cdot \epsilon \ \mathbf{k}' \cdot \mathbf{k})/4$$

$$+i(-F_2'^1 - 4F_2'^3)S(z \cdot (\epsilon' \times \epsilon) \ \mathbf{k}' \cdot \mathbf{k})/2$$

$$+(-F_2'^2 - 7F_2'^4)S(\epsilon' \cdot z \ \epsilon \cdot z \ \mathbf{k}' \cdot \mathbf{k})/2$$

$$+(-2F_2'^2 - 8F_2'^4)S(z \cdot (\epsilon' \times \epsilon) \ z \cdot (\mathbf{k}' \times \mathbf{k}))/4$$

$$+3iF_2'^3S(\epsilon' \cdot z \ \epsilon \cdot z \ z \cdot (\mathbf{k}' \times \mathbf{k}))/2$$

$$+6F_2'^4\epsilon' \cdot z \ \epsilon \cdot z \ \mathbf{k}' \cdot z \ \mathbf{k} \cdot z$$

(19)

where the expression $S(t)$ means the symmetrised expression formed by the term t plus the other three derived terms that one obtains swapping ϵ' with $\mathbf{k}'$ and/or ϵ with $\mathbf{k}$. Our formula for quadrupolar scattering is in agreement with Hill & McMorrow one[3].

4 Non spherical case.

In this section we develop a phenomenological formalism for resonant magnetic scattering in the non-spherical case. Our starting point is crystal-field theory where the non sphericity of the atomic environment is represented by a one-particle mean field potential which is added to the atomic Hamiltonian. Such an approach, pioneered by the works of Bequerel[5], Bethe[6], Kramers[7] and van Vleck[8], was applied to the calculation of x-ray absorption spectra and scattering factors for the first time by van der Laan and Thole[1].

The crystal field T is given by a superposition of spherical tensors :

$$T = \sum_{l,q} t_{l,q} T_q^l \qquad (20)$$

The tensor T must be invariant under all operations of the point symmetry group of the system[2].

We treat perturbatively the crystal-field correction to scattering amplitude considering a process, in one-particle approximation, where an electron is promoted from a closed shell state, denoted by $|n_g l_g \frac{1}{2}; J_a j_z\rangle$, to the intermediate states $|n_a l_a m_{az}\rangle |\frac{1}{2}\sigma\rangle$ and $|n_b l_b m_{bz}\rangle |\frac{1}{2}\sigma\rangle$ of two opens shells (n_a, l_a) and (n_b, l_b). The perturbation T has matrix elements which mix the two shells.

We write the initial one-electron state, discarding some unessential labels, as:

$$|J_a j_z\rangle = \sum_\sigma c(j_z, \sigma)|\sigma > |l_g, j_z - \sigma > \qquad (21)$$

where $c(j_z, \sigma)$ stands for the Clebsh-Gordon coefficient $c(l_g, j_z - \sigma, 1/2, \sigma; J_a, j_z)$.

The electron-photon interaction is represented by the tensors $P' = P(\epsilon', \mathbf{k}')$ for the outgoing photon, and P for the incoming one.

The scattering amplitude at first order in T takes the form :

$$\sum_{m_{gz}} \sum_\sigma c_{(m_{gz}+\sigma,\sigma)}^2 \sum_{qq'} < l_g, m_{gz}|P_b'^*|l_b, m_{gz} + q' > \times$$

$$f_{b(m_{gz}+q',\sigma)} < l_b, m_{gz} + q'|T|l_a, m_{gz} + q > \times$$

$$f_{a(m_{gz}+q,\sigma)} < l_a, m_{gz} + q|P_a|l_g, m_{gz} >$$

$$+[a \leftrightarrow b] \qquad (22)$$

In this expression the factor $f_b(m, \sigma)$, or $f_a(m, \sigma)$, contains implicitly the electron propagator for the spherical atom and accounts also for the orbital occupancies.

$c^2(m_z + \sigma, \sigma)$ for L_3	$m_z = 1$	$m_z = 0$	$m_z = -1$
$\sigma = 1/2$	1	2/3	1/3
$\sigma = -1/2$	1/3	2/3	1

Table 1. values of $c(j_z, \sigma)$ at the L_3 resonance

Starting from this expression we can arrive at a contracted form which contains, beside polarisation vectors and the magnetisation axis, the T tensor representing the crystal field, and the spherical tensors $T^{l_g}_{m_z}$ representing the core state. The perturbative process concerns intermediate levels of well defined angular moment l_a and l_b. This imposes a restrictions on the possible contractions : the transition due to a P tensor from the $L = l_g$ ground state to the $L = l_n$ excited levels implies that exactly $(l_g + rank(P) - l_n)/2$ contractions must be taken between the tensor and the inital ground state. Our one-particle approximation neglects the energy spread of the intermediate states due to many-body effect and is therefore similar to the fast-collision approximation employed by Marri and Carra for the case of dipole-quadrupole scattering in a magnetoelectric crystals[9].

We develop $f_a(q, \sigma)$ and $f_b(q, \sigma)$ in powers of L_z, as in the previous section :

$$f(q, \sigma) = \sum_n f_{n,\sigma} q^n \to \sum_n f_{n,\sigma} L_z^n \qquad (23)$$

The scattering amplitude is then written as :

$$\sum_{m_{gz}, \sigma, n_a, n_b} f^b_{n_b, \sigma} f^a_{n_a, \sigma} c^2_{(m_{gz} + \sigma, \sigma)}$$

$$\mathbf{C}(T^{l_g *}_{m_z} P'^*_b |^{\leftarrow} (i\xi_m \times)^{n_b} T^{l_g}_{m_z} (i\xi_m \times)^{n_a} P_a |^{\to} T^{l_g}_{m_z})$$

$$+ symm. \qquad (24)$$

where the expression is symmetrised by the following substitutions:

$$symm. = [a \leftrightarrow b]$$

and the symbol $|^{\leftarrow}$ ($|^{\to}$) following a polarisation tensor means that the number of contractions of such tensor with the preceding (following) ground level tensorial object is constrained as discussed above. The $(i\xi_m \times)$ operator operates on all the object at its right (remember that $(i\xi_m \times) A \, B = ((i\xi_m \times) A) \, B + A \, ((i\xi_m \times) B))$.

A formal derivation of these contraction rules is given in appendix A.

As an example we give a specialised expression for the L_3 edge. We give in table 1 the coefficients $c^2(j_z, \sigma)$. It is useful to notice that for a given $m_z = j_z - \sigma$ the sum of two coefficients of opposite spin is constant and equal to $4/3$, while the difference goes from $-2/3$ to $2/3$ with a linear dependence on m_z. This behaviour does not depend on the particular edge that we have considered. In general, for an edge e, we can always write : $c^2(m_z + \sigma, \sigma) = l_e + 2 s_e \, \sigma m_z$ where l_e and s_e are constants which depend on the edge. For example, at L_3, we have $l_e = 2/3$ and $s_e = 1/3$, while at L_2 $l_e = 1/3$ and $s_e = -1/6$.

It is then useful to rewrite equation 24 as :

$$l_e \sum_{n_a, n_b} \tfrac{2}{3} (f^b_{n_b, 1/2} f^a_{n_a, 1/2} + f^b_{n_b, -1/2} f^a_{n_a, -1/2}) \times$$

$$\sum_{m_{gz}} \mathbf{C}(T^{l_g *}_{m_z} P'^*_b |^{\leftarrow} \quad (i\xi_m \times)^{n_b} T^{l_g}_{m_z} (i\xi_m \times)^{n_a} P_a |^{\to} T^{l_g}_{m_z})$$

$$+ s_e \sum_{n_a, n_b} \tfrac{1}{3} (f^b_{n_b, 1/2} f^a_{n_a, 1/2} - f^b_{n_b, -1/2} f^a_{n_a, -1/2}) \times$$

$$\sum_{m_{gz}} \mathbf{C}(T^{l_g *}_{m_z} P'^*_b |^{\leftarrow} (i\xi_m \times)^{n_b} T^{l_g}_{m_z} (i\xi_m \times)^{n_a} P_a |^{\to} (i\xi_m \times) T^{l_g}_{m_z})$$

$$+ symm. \qquad (25)$$

In the second term we have converted the m_z quantization number into the operator $(i\xi_m\times)$ at the left of the core-hole orbitals. Once contracted, the above formula gives in the general case a complicated expression.

However for terms which are zero and first order in $(i\xi_m\times)$, the sum over core-hole orbitals can be simplified in an elegant way.

The zero order terms describe anysotropy of the crystal field. The first order one describe crystal field induced corrections to the magnetic scattering.

Concerning the zero order terms, we notice that such sum looks like a trace. In other words if, in a given contraction diagram, a vector A is contracted with the *ket* ground orbital, and another vector B is contracted with the same *bra* core orbital the result is equivalent to a contraction of A with B because the sum runs over a complete basis of an irreducible supbspace.

Concerning the first order terms, $(i\xi_m\times)$ operates either on the core-hole orbital, or on the intermediate tensors (P, P', and crystal field tensor T).

The terms where $(i\xi_m\times)$ operates on the intermediate tensors can be simplified as in the zero order case described above.

Now we consider the terms where one $(i\xi_m\times)$ operates on the core-hole orbital. The contraction diagrams arising from these terms can be split in two classes.

In the first class $(i\xi_m\times)$ operates on a core-hole vector and the result is contracted with another core-hole vector. This class gives zero contribution because $(i\xi_m\times)$ is an antisymmetric operator.

The second class is given by the remaining terms which contain the factor $\mathbf{v}\cdot((i\xi_m\times)\mathbf{h})$, where $\mathbf{v}$ is a vector which enters the composition of an intermediate tensors and $\mathbf{h}$ enters the composition of the core-hole tensor. This factor can be rewritten as $-((i\xi_m\times)\mathbf{v})\cdot\mathbf{h}$ and once again the sum over the core-hole orbitals disappear from the final expression.

The general expression for scattering amplitude, up to first order in $(i\xi_m\times)$ is therefore :

$$\sum_{n_a,n_b=0}^{n_a+n_b=1} a_{n_a,n_b} \times$$
$$\mathbf{C}(P_b'^* \, (i\xi_m\times)^{n_b} T_{m_z}^{l_g} (i\xi_m\times)^{n_a} P_a)$$
$$+symm. \tag{26}$$

where the a_{n_a,n_b} depends linearly on the f electron propagators and the exact linearity coefficients can be found working out the contraction diagrams.

For higher order terms this simplification is no more appliable in the same easy way. One could still write contractions where the core-hole tensor disappear but the formula would be complicate by the fact that when one rewrites $\mathbf{v}\cdot((i\xi_m\times)^2\mathbf{h})$ as $((i\xi_m\times)^2\mathbf{v})\cdot\mathbf{h}$, the $(i\xi_m\times)^2$ operator cannot be factored out of the tensor composed by v because

$$(i\xi_m\times)^2(\mathbf{v_1}\,\mathbf{v_2}) \neq ((i\xi_m\times)^2\mathbf{v_1})\,\mathbf{v_2} + \mathbf{v_1}\,((i\xi_m\times)^2\mathbf{v_2})$$
$$\tag{27}$$

The core orbital disappears from the final expression because, in our approximation, our L_3 core state in Eq. 21 is not coupled to the valence orbitals. Such an approxima-

tion is valid for the hard x-rays domain where the core-hole is deep.

For the sake of simplicity, in the following, examples we limit ourself to consider only zero and first order contributions.

4.1 Application :Magnetic diffraction amplitude for spiral antiferromagnetic holmium

We consider the case of holmium. The holmium crystal has a hcp structure where the atoms are embedded in a local D_{3h} symmetry environment.

Taking a cartesian x, y, z frame with x along the hcp a axis :

$$T = t_2(3z^2 - (x^2 + y^2 + z^2)) \pm t_3(x^3 - 3xy^2) + \ldots \quad (28)$$

where the first omitted term of the serie is a rank 4 component. The $\pm$ signs alternate from one ab plane to the other.

The contribution of the $(2z^2 - x^2 - y^2)$, is centrosymmetric. So we consider separately the dipole-dipole and the quadrupole-quadrupole scattering. Within the framework of our simplifying assumption (equation 26) we find that the dipole-dipole scattering correction is proportional to

$$3\epsilon' \cdot \mathbf{z} \, (i\hat{\xi}_m \times \epsilon) \cdot \mathbf{z} - \epsilon' \cdot (i\hat{\xi}_m \times \epsilon) - [\epsilon' \leftrightarrow \epsilon] \quad (29)$$

The second term of this expression merges with the previously found form for the scattering in the spherical approximation. But the first term contains two scalar products with the $\mathbf{z}$ axis and this adds complexity to the amplitude dependence on experimental geometry.

The quadrupole-quadrupole scattering, discarding those terms that can be merged with the spherical formulas, has the form :

$$\{\{\{\{$$
$$(\mathbf{k}' \cdot \hat{z})(\mathbf{k} \cdot \hat{z})\epsilon' \cdot (i\hat{\xi}_m \times \epsilon)$$
$$+ [i\hat{\xi} \times \epsilon \leftrightarrow \mathbf{k}] \ \} + [\mathbf{k} \leftrightarrow \epsilon] \ \} + [[\mathbf{k}' \leftrightarrow \epsilon']] \ \}$$
$$- [\mathbf{k}, \epsilon \leftrightarrow \mathbf{k}', \epsilon'] \ \}$$

$$(30)$$

this term also contains two scalar products with the $\mathbf{z}$ axis adding complexity to the amplitude dependence on experimental geometry.

These terms contribute, in our system, to the amplitude of the $2n \pm q$ Bragg orders diffraction peaks, n and q being the antiferromagnetic wavevectors. In an experiment which measures several $2n \pm q$ Bragg order diffraction peaks, the incidence angle may vary considerably from one order to the others, and therefore we predict that the inclusion of our correction could improve the fit.

The scattering factor contribution from the alternating term $\pm(x^2 - 3xy^2)$ gives diffraction peaks at $2n + 1 + mq$ orders, n and m being integers and q being the antiferromagnetic wavevector. To simplify the following treatement, and to give an example of a term contributing to the $2n+1+q$ scattering, we consider magnetisation in the xy plane and we limit here to the case where, in equation 26, only the $n_a = 1$, $n_b = 0$ term is considered. We apply the contraction rules to formula 26 where P' and P are ϵ and $\mathbf{k} \otimes \epsilon$ tensors respectively. In this we get case a

scattering amplitude proportional to :

$$(($$

$$-6i(\epsilon' \cdot \hat{x})(\epsilon \cdot \hat{x})\hat{\xi}_m \cdot (\hat{x} \times k)$$

$$+6i(\epsilon' \cdot \hat{x})(\epsilon \cdot \hat{y})\hat{\xi}_m \cdot (\hat{y} \times k)$$

$$+6i(\epsilon' \cdot \hat{y})(\epsilon \cdot \hat{x})\hat{\xi}_m \cdot (\hat{y} \times k)$$

$$+6i(\epsilon' \cdot \hat{y})(\epsilon \cdot \hat{y})\hat{\xi}_m \cdot (\hat{x} \times k)$$

$$) + [\epsilon \leftrightarrow k]$$

$$) + [k \leftrightarrow k', \epsilon \leftrightarrow \epsilon']$$

$$(31)$$

5 Conclusions

We have established a contraction method by which we obtain phenomenological analytical expressions for the scattering factors in terms of scalar and vectors products of the polarisation vectors, of the magnetisation axis and of the vectors defining the crystal field tensor. Using a perturbative approach we have been able to go beyond the usual $SO2$ approximation [3] considering simultaneaously the magnetisation and a general crystal field tensor. Our method is a viable diagrammatic technique based on contraction between vectors. With our method useful formula can be straightforwardly obtained in terms of the polarisation vectors, the crystal field vectors and the magnetisation direction.

We have applied the method to the case of holmium, giving the crystal field correction for the quadrupole-quadrupole scattering and predicting dipole-quadrupole peaks occurring at $2n + 1 + mq$ Bragg orders. Our work completes the Hill & McMorrow one[3].

7 Appendix A: derivation of contraction rules

We show in this section how an angular integration of a polynomial over a unit sphere surface can be expressed as a sum of contraction diagrams.

The polinomial integration that we consider is :

$$\int_S (\prod_i^{2N} \mathbf{a}_i \cdot \mathbf{n}) dn^2 \qquad (32)$$

where $2N$ is the polynomial order, $\mathbf{a}_i$ are vectors, and bfn is a unit vector. By multiplying and diving this expression by $\int exp(-r^2) r^{2N+2} dr$ we transform it into an integral

over the whole space:

$$\int_S (\prod_i^{2N} \mathbf{a}_i \cdot \mathbf{n}) dn^2 =$$

$$\int (\prod_i^{2N} \mathbf{a}_i \cdot \mathbf{r}) exp(-r^2) d\mathbf{r}^3/(\Gamma(N+3/2)/2) =$$

$$\prod_i^{2N} \mathbf{a}_i \cdot \partial_\mathbf{v}(\int exp(-r^2 + \mathbf{v} \cdot \mathbf{r}) d\mathbf{r}^3)|_{v=0}/(\Gamma(N+3/2)/2) =$$

$$\prod_i^{2N} \mathbf{a}_i \cdot \partial_\mathbf{v} \, exp(\mathbf{v}^2/4)|_{v=0}\Gamma(3/2)/\Gamma(N+3/2)$$

$$(33)$$

In this expression, when $v = 0$ only the terms fully contracted remain because if $\mathbf{a}_l \cdot \partial_\mathbf{v}$ takes down a $\mathbf{v}/2$ factor from the exponent, another $\mathbf{a}_m \cdot \partial_\mathbf{v}$ must be used to derive this $\mathbf{v}/2$ factor which otherwise gives zero contribution, and this gives the scalar product $\mathbf{a}_l \cdot \mathbf{a}_m$.

The intermediate sum which appear in equation 22, can be considered as a projector p_{l_a} over a tensorial space of definite rank l_a. The projection over definite rank space is obtained through the $|^\leftarrow$ and $|^\rightarrow$ constraint. When applying contraction rules to expressions formed by tensor of a defined rank, one must bear in mind that, by definition, a defined rank tensor gives zero when contracted with itself.

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